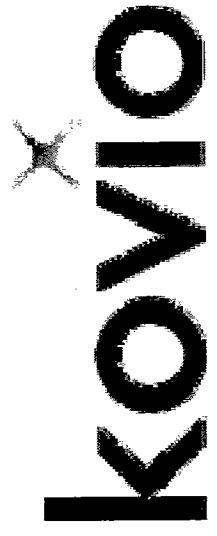


# **EXHIBIT A**



## Nanocrystalline Silicon Ink

Fabio Zurcher, Brent Ridley, Joerg Rockenberger  
[redacted]

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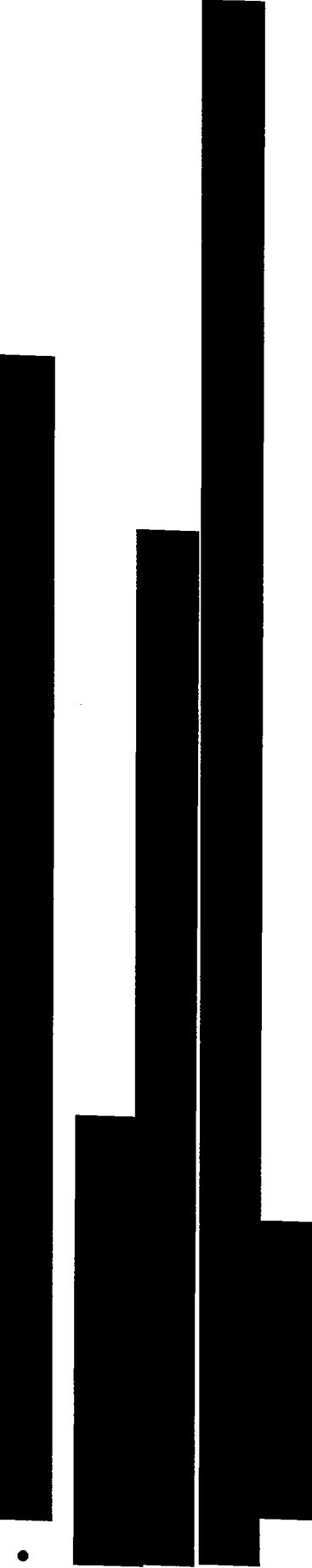
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nc-Si Project

# Project Weekly Report

## Big Picture Objective

- Formulate Ink of Hydrogen-Capped Silicon-Nanocrystals (nc-Si:H)



## Key Results

- [REDACTED] Amines, Esters, Amides, Polyethers + Anionic Surfactants Good; All Solvents Can Yield "Stable, Milky" Dispersions of nc-Si:H
- Tested 16 Surfactants in Xylene With High-Power Ultrasound: 3 Show Almost Clear, Yellow "Solutions" Of nc-Si:H After 0.5 Micron Filtration.



NC-SI:H - DEVELOPMENT PLAN

STEP	PURPOSE	EXPERIMENTS	OS	Done
Solvent Screen	1. determine compatibility of nc-Si:H w/ various solvents	1. Ultrasonicate nc-Si:H powder in solvent; check oxidation w/ FTIR		
Surfactant Screen	1. Determine miscibility of surfactants w/ solvents	1. 1% surfactant solution; optical inspection		
Dispersion Screen	1. determine suitability of solvents + surfactants to disperse nc-Si:H	1. Ultrasonicate 1% surfactant solvent solution w/ 0.1% nc-Si:H; Optical inspection + filtration		
Ink Formulation	1. Formulate 5 wt% Si-NC:H ink	1. Refine formulation recipe varying agitation parameters, surfactant conc. etc.		

## Project Is On Track:

- Dispersion Screen Is Finished
- [REDACTED]
- Evaluated 650+ Formulations so far...

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# Risks Map

Issue	Mitigation Plan	Risk
Agglomerate Size Bigger than 20 nm	<ul style="list-style-type: none"> <li>• Higher Ultrasound Power (smaller tip)</li> <li>• Longer Ultrasonication Times</li> <li>• Increased Surfactant Concentration</li> <li>• Apply Ultrasonication + Surfactant During Etch</li> <li>• Separate Larger Agglomerates By Centrifugation + Filtration</li> <li>• Use Multidentate Surfactants</li> <li>• Let's do photovoltaics...</li> </ul>	H
Very Low Mass Loading (< 0.1 %)	<ul style="list-style-type: none"> <li>• Drop-Casting Instead Of Spin-Coating</li> <li>• Increased Surfactant Concentration</li> <li>• Higher Ultrasound Power (smaller tip)</li> <li>• Longer Ultrasonication Times</li> <li>• Apply Ultrasonication + Surfactant During Etch</li> <li>• Use Multidentate Surfactants</li> </ul>	H
Colloidal Stability	<ul style="list-style-type: none"> <li>• Increased Surfactant Concentration</li> <li>• Use Multidentate Surfactants</li> </ul>	H
Inpurity Levels	<ul style="list-style-type: none"> <li>• Keep Surfactant Concentration As Low As Possible</li> <li>• Choose Small-Molecule Surfactants</li> <li>• Oxygen-Free Surfactants</li> </ul>	H
Film Density	<ul style="list-style-type: none"> <li>• Keep Surfactant Concentration As Low As Possible</li> <li>• Choose Small-Molecule Surfactants</li> </ul>	H

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# 3rd Screen: Dispersion Of nc-Si:H

## Goals:

- Identify Surfactants + Solvents Which Can Disperse nc-Si:H During Ultrasonication

### 3. Screening Summary

Surfactants	#	Solvents						DMSO	Toluene	Ethyl ethoxy	Anisole	Limonene	DHT acetate	1-Dodecene
		Butyl ether	Xylene	Decaline	Diglyme	Tetrahydrofuran	Propionate							
Tridecylamine	1	?	?	?	?	?	?	?	?	?	?	?	?	?
Dimethylidodecylamine	2	?	?	?	?	?	?	?	?	?	?	?	?	?
Thiourea	3	?	?	?	?	?	?	?	?	?	?	?	?	?
N,N-Dimethyldecylamide	39	?	?	?	?	?	?	?	?	?	?	?	?	?
Sorbitol monooctate	4	?	?	?	?	?	?	?	?	?	?	?	?	?
Unilever's methyl ester	5	?	?	?	?	?	?	?	?	?	?	?	?	?
SDS	6	?	?	?	?	?	?	?	?	?	?	?	?	?
Union X-100	7	?	?	?	?	?	?	?	?	?	?	?	?	?
Union X-114	8	?	?	?	?	?	?	?	?	?	?	?	?	?
Union XL-80N	9	?	?	?	?	?	?	?	?	?	?	?	?	?
Genal CO 630	21	?	?	?	?	?	?	?	?	?	?	?	?	?
Genal CO 520	4	?	?	?	?	?	?	?	?	?	?	?	?	?
gena CO 621	22	?	?	?	?	?	?	?	?	?	?	?	?	?
Conethylene glycol monooctate	17	?	?	?	?	?	?	?	?	?	?	?	?	?
Wepa 60	18	?	?	?	?	?	?	?	?	?	?	?	?	?
Wepa 30	19	?	?	?	?	?	?	?	?	?	?	?	?	?
Acetone	20	?	?	?	?	?	?	?	?	?	?	?	?	?
Dimethylsulfide	10	?	?	?	?	?	?	?	?	?	?	?	?	?
Upol A	13	?	?	?	?	?	?	?	?	?	?	?	?	?
Vinol OI	14	?	?	?	?	?	?	?	?	?	?	?	?	?
Rhodoclear ER	23	?	?	?	?	?	?	?	?	?	?	?	?	?
Spesso 52MS	27	?	?	?	?	?	?	?	?	?	?	?	?	?
Spesso 10A503	28	?	?	?	?	?	?	?	?	?	?	?	?	?
Dispersant KS 8/33M	29	?	?	?	?	?	?	?	?	?	?	?	?	?
Dispersant 10/1004	30	?	?	?	?	?	?	?	?	?	?	?	?	?

Legend:  
■ = "good" (milky)  
■ = "ok" (turbid or flakey)  
■ = bad (precipitated or reacted)

PEP = poly ethylene oxide  
PEP = poly "methyl ethylene oxide (propyl oxide)  
scrb = sorbito derivat.

## Main Conclusions:

- Solvent: everything works  $\Rightarrow$  concentrate on xylene
- Surfactant: amines, PEO, esters, amides + anionic work

# nc-Si:H Ink Formulation

## Goals:

- Identify Surfactant Suitable For Dispersion of <0.5 Micron nc-Si:H Agglomerates In Xylen

Surfactant	Affter centrifugation	Filtration	Affter FT-IR Oxidation <sup>2</sup>
Hexadecylamine		pale yellow	
Dimethyldecylamine			
Trioctylamine			
4-Dodecyldiethylbenzylamine	yellow SN	pale yellow	yellow
N,N-Diethyldecanamide	pale yellow SN	pale yellow	pale yellow
Sorbitan monooleate		n/a	
Linoleic acid ethyl ester	pale yellow SN		
C12E5		faint yellow	
Triton X-100		faint yellow	
Triton X-114			
Triton Xl-80N			
Igepal CO 210			
Igepal CO 520			
Addid 130		n/a	
K-Sperse 152/MS		pale yellow	
Disparion KS-873N dispersing agent	Yellow/orange SN	yellow	yellow
	Yellow/orange SN	yellow	
			colored, transparent milky

## Main Conclusions:

- 3 Formulations give yellow, mostly transparent solutions after 0.5 micron filtration
- 2 are anionic surfactants!!!! How does that work???
- Si-Mass loading estimated to be ~0.01%  $\Rightarrow$  Surfactant-Si mass ratio: 500

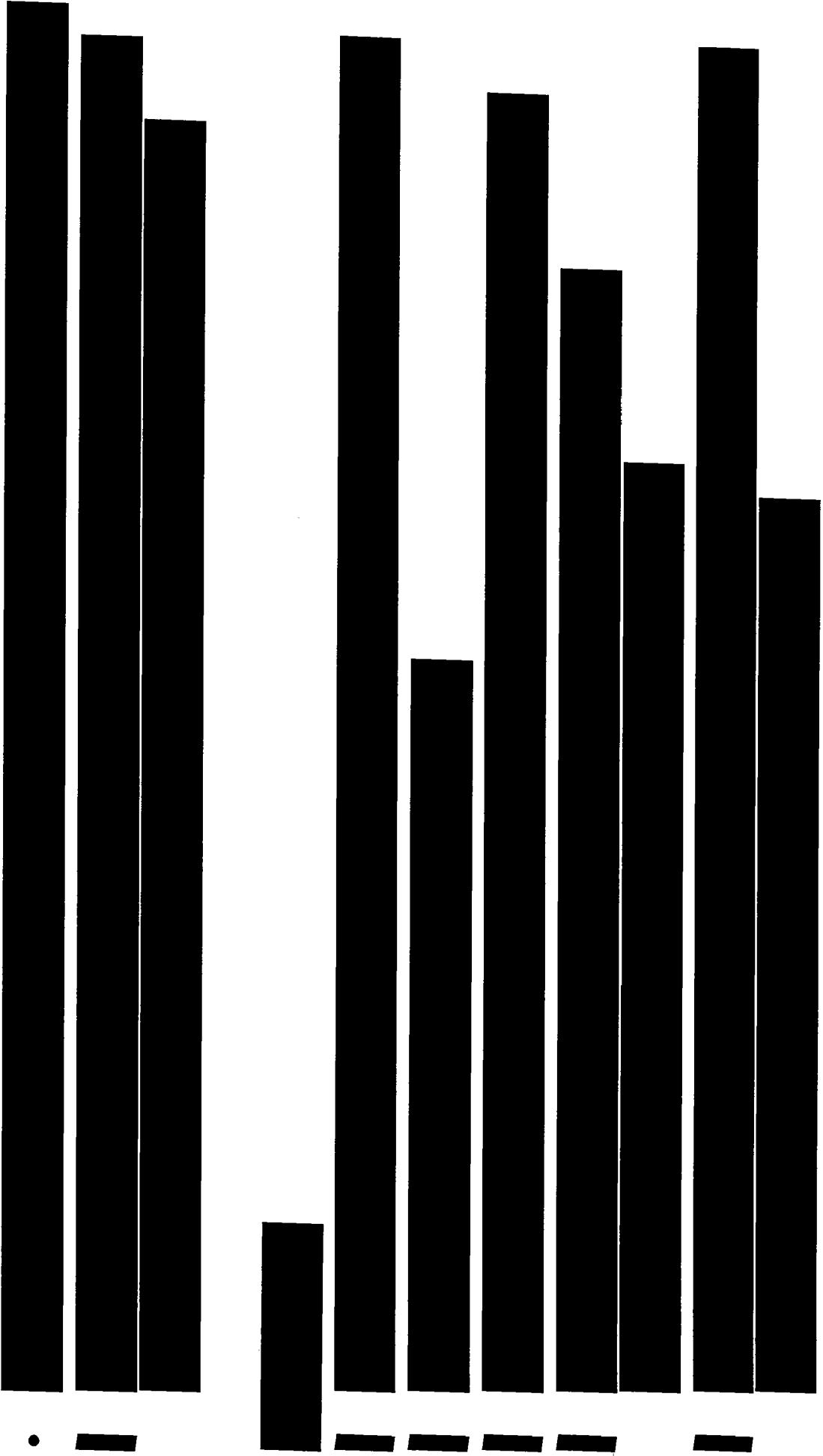
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# Results

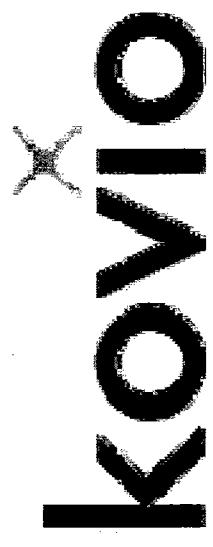
- All Solvents Can Yield Milky Dispersions of nc-Si:H
- Amines, Polyethers, Esters, Anionic Surfactants “Work”
- 



# Milestone Weekly Schedule – nc-Si

Crit Path	Milestone	Who	Start	OS	CS	Done?	Comments
nc-Si	FTIR + TEM of Supernatants	BR/FZ	08/19	08/21			verfiy identity of supernatants
nc-Si	Sonication of Surfactants + Solvents as Control	FZ	08/20	08/21			verfiy identity of supernatants
nc-Si	search for multidentate + polymeric amines	FZ/BR	08/18	08/25			
nc-Si	DOE on sonication: power, time, surfactant concentration	FZ/BR	08/19	08/25			
nc-Si	Screen surfactants in pyrdine	BR	08/20	08/23			

## **EXHIBIT B**



# Surface Derivatization of Silicon Nanocrystals

Fabio Zurcher, Brent Ridley  
[REDACTED]

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# Pros & Cons of the AIBN Reaction

Pros	Cons
<ul style="list-style-type: none"><li>Short reaction time (30min)</li><li>Reliable reaction</li><li>No obvious source of metal or halogen contamination</li><li>Reliable and relatively simple isolation/purification step</li><li>Product is a well defined, dry powder</li><li>Product is very soluble in hydrocarbons and ethers</li></ul>	<ul style="list-style-type: none"><li>Product shows reoxidation</li><li>Yield is not exceptionally high</li><li>AIBN byproducts are difficult to remove</li><li>Product is not extremely soluble in aromatics</li></ul>

# Derivatization Reaction Flow

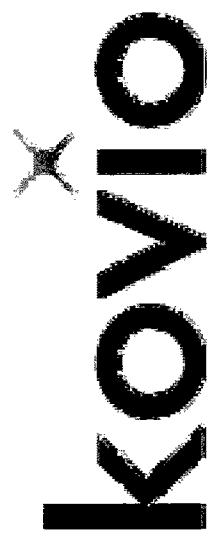
Step	Description
Derivatization	<p><b>nano-Si stock (etch product suspended in xylene) + dodecene + AIBN + solvent (xylene).</b></p> <p>[dodecene] = 1M; [Si] = 0.25M; [AIBN] = 0.1M</p> <p>T = 120°C t = 30min</p>
Filtration	<p><b>Reaction product is filtered hot through a 0.2μm PTFE filter</b></p>
Precipitation	<p><b>Product is precipitated with cold MeOH and centrifuged to remove the SN</b></p>
Wash	<p><b>The precipitated product is washed with AcN to remove residual AIBN byproducts and then centrifuged</b></p>
Dry	<p><b>The remaining solid is dried overnight under Ar or N<sub>2</sub> flow</b></p>

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## **EXHIBIT C**



# Silicon Film Formation From Nanocrystals

Joerg Rockenberger, Fabio Zurcher, Brent Ridley  
[REDACTED]

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Silicon Film Formation from Nanoparticles

# Surface-Modified Si Nanoparticles

		AIBN	AlEtCl2
Synthesis:	Si-NC production [mg/batch]	30	90
	Synthesis + Isolation Time [h]	3	72
	Temperature [C]	120	40
Ink Formulation:	Oxygen – Level [%]	0.5	0.1 – 0.2
	TGA – Mass Loss [%]	20	TBD
	Solubility – Xylene [%]	TBD	5%
Film Characterization:	Solubility – Butylether [%]	> 5%	< 1%
	Oxygen – Level [%]	15 / 11	21
	Carbon - Level [%]	15 / 18	17
SEM - Morphology	Hydrogen – Level [%]	18	TBD
	SEM – Thickness [nm]	150 – 250	0 - 100
	XRD – Grain Size [nm]	TBD	very rough – waffle
Tencor – Thickness [nm]	Tencor – Thickness [nm]	150 -250	85
	Tencor – Roughness [nm]	< 2	6

**BIGGEST DIFFERENCE: RELATED TO SOLUBILITY + RESULTING FILM MORPHOLOGY!**

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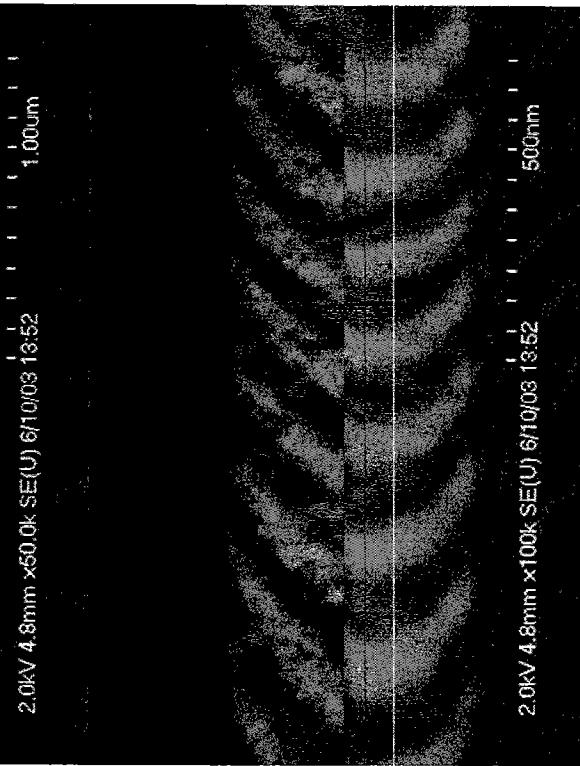
Si Film Formation from Nanoparticles

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# Surface-Modified Si Nanoparticles

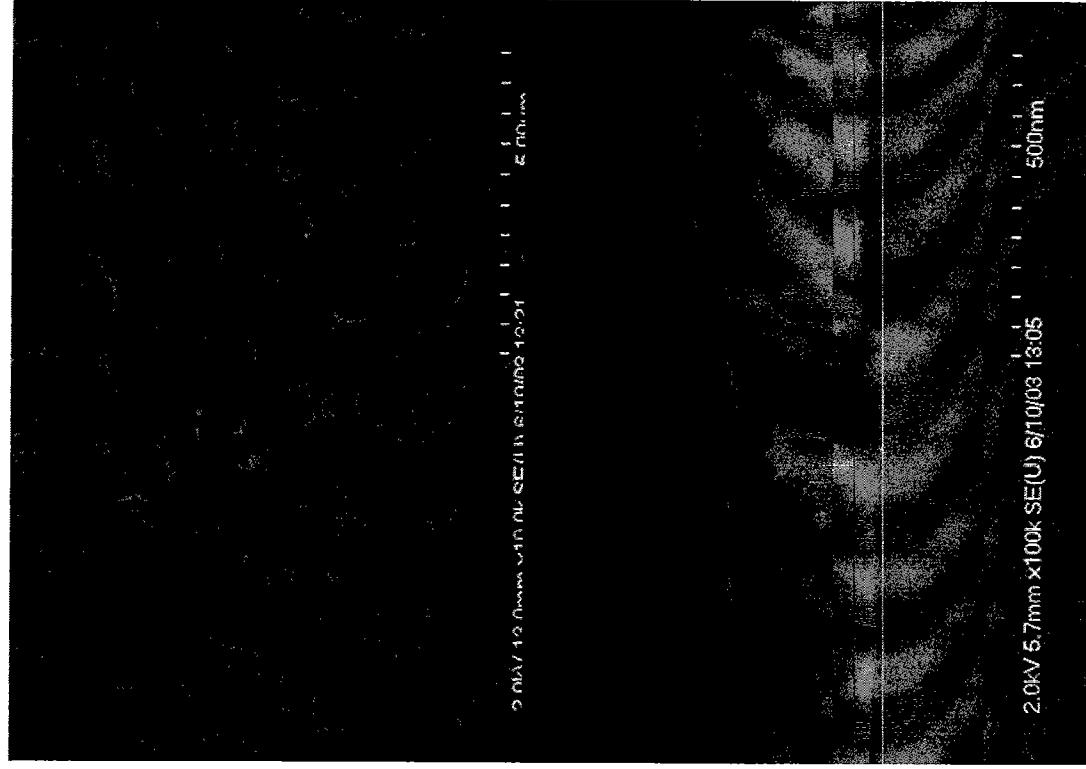
## AIBN Reaction

5% in Butylether, 300 rpm  
100 C softcure, 900 C hardcore



## Lewis Acid Reaction

2% in Xylene, 300 rpm  
100 C softcure, 500 C hardcore



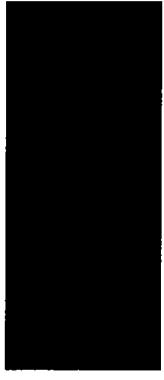
**Si Film Formation from Nanoparticles**

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## **EXHIBIT D**

# *Polysilane ink formulation*



# Polysilane ink formulation

## Goal

- Find solvents that are compatible with cyclosilane.
- Reproducibly provide a polysilane ink formulation with a shelf life of > 1 day.

Module	Experiments
Ink formulation stability	Test cyclosilane compatibility in different solvents
	2. Thermally polymerize cyclosilane <ul style="list-style-type: none"><li>– FTIR</li><li>– Solubility in cyclosilane, cyclooctane</li></ul>
	3. UV polymerize cyclosilane at RT <ul style="list-style-type: none"><li>– FTIR</li><li>– Solubility in cyclosilane, cyclooctane</li><li>– Weight loss</li></ul>

# Silane Compatibility With Solvents

Linear Alkanes	Cyclic alkanes	Alcohols/Ketones/Enes	Aromatics	Ethers	Fluoro
Decane	Cyclonexane	$\alpha$ -Terpineol	Benzene	Dicyanette®	Fluorinert FC 70
Tetradecane	Cycloneptane	DHT	Toluene	Butylether	Perfluoro(1-methyl)decaline
	Cyclooctane	1-Methoxy-2-propanol	O-xylene	Anisol	Fluorinert FC 70 + Perfluoroctansulfonylfluoride
	Cyclodecane (tbd)	$\alpha$ -Pinene	Mesitylene		
	Methyl-cyclohexane	2-Butanone	t-Butyl-toluene		
	t-Butyl-cyclohexane	2-Heptanone	Cyclohexylbenzene		Stable > 2 days
	trans-decaline	Cyclopentanone	Tetraline		Limited stability white ppt.
	Bis-cyclohexyl	Ethylpyruvate			white ppt., then dissolution two phases
	Butylether				

# Polysilane ink formulation

Sources that may have an impact on ink stability	Parameters for experimental matrix
Light or temperature induced polymerization	Temperature: ~0C, 45C Light/dark: dark at 0C, clear/amber glass vials at 45C
Solvent purity (water and other impurities)	Distill and dry Cyclooctane, cis-decaline
OH (leaching from glass wall) induced polymerization	Teflon vials and silanized glass vials
Contamination from tips, cap lining	Use current pipettor tips, cap lining
Nature of silane mixture, SiH <sub>3</sub> groups as radical initiators)	Silane batch: fixed, █ 21-1A, needed: 30 x 30 uL = 900 uL; NMR control of cyclosilane/cyclohexane ink
Mass loading	Concentration: fixed, 20 vol%, Amount: fixed, 150 uL
Nature of solvent	Solvent: Cyclohexane, Cyclooctane, (Cycloheptane), Ether, toluene, (cyclododecane), decaline █ █
	█ █

## **EXHIBIT E**

**kovio**

## Silane Ink Formulation

# Solvent Selection and Controlled Polymerization

Silane Ink Formulation

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# Solvent/Silane Compatibility

Solvent	bP (°C)	V (cP)	S (mN/m)	Cutoff (nm)	Solubility	FTIR	Thin Film
<b>Alkanes/Aromatics</b>							
Cyclooctane	151	1.0			OK	No Si-O	
cis-Decalin	193	3.0			OK	No Si-O (100 °C)	UV Film OK
Decalin (mixture)	191	2-3			OK		
<i>o</i> -Xylene	144	0.8	29.5		OK	No Si-O (100 °C)	
Tetralin	207	2.1			OK		
Methylnaphthalene	240	3.1			OK	No Si-O (150 °C)	
Tetradecane	252	2.1			Cloudy→OK	No Si-O (150 °C)	
<b>Exotics</b>							
D4 Cyclomethicone		2.4	17.4		OK	No Si-O (150 °C)	
D5 Cyclomethicone		3.8	17.4		OK	No Si-O (150 °C)	
Cineole*		176	2.3		OK→Solids	No Si-O (100 °C)	
EG-dibutylether	203	14			OK→Solids		
3-Octanol*	174	7			Cloudy	Oxidation	
2-Ethyhexanol	182	4-6			Cloudy	Oxidation	
Dihydroturpene†	208	46			OK	Oxidation	
Dihydroturpene (FF)	208	46			OK→Solids		
Terpinen-4-ol*	212	12			OK	No Si-O (150 °C)	Film oxidation
Terpineol*	217	37	32		OK	No Si-O (150 °C)	Film oxidation
Pine Oil 60			5		OK	Oxidation	

\*Similar results after drying solvent over molecular sieves

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Silane Ink Formulation

# Silane Polymerization

Sample	Loading (vol%)	Solvent	Exposure (min)	Observation		FTIR (cast)
				UV	(solution)	
4-60-0	none	c-C <sub>8</sub> H <sub>16</sub>	5min	Clear	N/A	N/A
4-60-1	5%	c-C <sub>8</sub> H <sub>16</sub>	5min	Cloudy (from walls)	Good wetting/film	No change(s)
4-60-2	5%	<i>o</i> -xylene	5min	Clear (even walls)	Good wetting/film	No change(s)
4-60-3	5%	c-C <sub>8</sub> H <sub>16</sub>	20min	Clear	Good wetting/film	No change(s)
4-62-1	25%	c-C <sub>8</sub> H <sub>16</sub>	20min	Clear	Good wetting/film	No change(s)
4-62-2	25%	c-C <sub>8</sub> H <sub>16</sub>	60min	Milk	N/A	Broad, Baseline
4-63-1	25%	<i>o</i> -xylene	40min	Cloudy	Good wetting/film	Broadening
4-68-1	100%	none	20min	Clear, viscous		Broadening
4-68-2	100%	none	60min	Pale amber, viscous		
<b>Molecular Sieve</b>				Sieves		
4-58-1	5%	c-C <sub>8</sub> H <sub>16</sub>	none	Clear	Poor wetting/film	N/A
4-60-2N	5%	<i>o</i> -xylene	none	Clear	Poor wetting/film	N/A
4-58-1S	5%	c-C <sub>8</sub> H <sub>16</sub>	4days	Clear	Poor wetting/film	No change(s)

**White films form routinely form on walls above liquid level (from vapor)**

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Silane Ink Formulation

# Viscous Silane(s) Solubility

\* 10% solutions – all others 20%

# Silane Ink Formulation

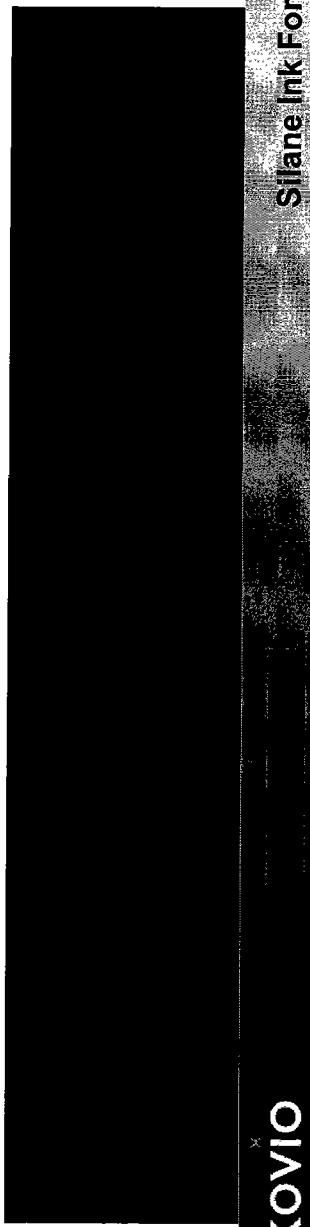
## Big Picture Objective:

- Formulate silane ink suitable for inkjet printing (viscosity, surface tension, etc.)
  1. Appropriate solvent selection
  2. Controlled silane polymerization
  - [REDACTED]
- Investigate alternatives to inkjet technology (microspot...)

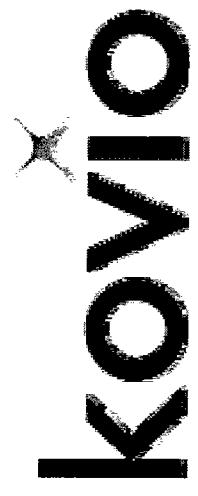


## Key Results:

- The viscous tertiary alcohol terpinen-4-ol is retained in UV-spun silane films and leads to oxygen and carbon loaded silane films after curing at 400 °C
- After drying over sieves, alcohol and ether solvents still cause problems with solubility and/or oxidation – so far, no solvents containing oxygen have worked except for the cyclomethicones
- UV polymerization reactions initiated – control of viscosity is underway [REDACTED], but polymerization (and precipitation) occurs in both cyclooctane and xylene solvents



## **EXHIBIT F**



# Solvent Compatibility Tables

## Technical Report

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# Activated Alumina Purification for Solvent Screen - █

## Purpose

- Purify inkjet solvent candidates and test solubility, stability, and printability

## Method

- Single-pass column purification of solvent – 9g activated alumina (500 °C under vacuum 6h), collecting 4mL fractions in amber vials after discarding first mL
- 20% solution using █ SOP polysilane

## Solvents

- Alkanes: Tetradecane, dicyclohexyl, decane, pinane, *t*-butylcyclohexane, isopropylcyclohexane, trimethylcyclohexane
- Aromatic: Methylnaphthalene, tetralin, cyclohexylbenzene
- Ethers: Diethylene glycol diethyl ether, dibutyl ether
- Halogenated: Chlorooctane, cyclohexyl chloride
- Silane: Tetraethylsilane

## Analysis Proposal

- Suggested testing, in order of execution: miscibility and solubility at 50% and 20%, stability at 20%, viscosity, contact angle, printability, NMR, GC-MS

## Results

- All 15 solvents were poor solvents for polysilane!
- Most were turbid solutions or two phase mixtures
- Some solvents formed two clear phases – tetradecane, decane
- **What makes *cis*-decalin and cyclooctane (and cyclooctane) so good?**

# Solvent/Silane Compatibility - 2004

Solvent	bP (°C)	$\eta$ (cP)	$\gamma$ (mN/m)	Solubility (5-10 vol%)	FTIR	Thin Film
Cyclooctane	151	2.2		OK		
Nonane	151	0.6	25	OK → Precip		TFTs
Decane	174	0.8	23	OK → Precip		
Decalin (mixture)	<b>191</b>	2.2	<b>32</b>	OK		
cis-Decalin	193	3.0	<b>32</b>	OK	No Si-O (100 °C)	TFTs
Cyclodecane	<b>201</b>	<b>4.3</b>		OK	No Si-O (150 °C)	
Dicyclohexyl	207	3.3		OK*		
Dodecane	216	1.2	25	OK → Precip		
Tetradecane	252	1.9		Cloudy → OK *	No Si-O (150 °C)	
<i>o</i> -Xylene	144	0.8	30	OK*	No Si-O (100 °C)	
1,2 Dichlorobenzene	180	1.3	<b>37</b>	Cloudy → OK *	No Si-O (150 °C)	
Tetralin	207	2.1	<b>33</b>	OK*	No Si-O (100 °C)	
MethylNaphthalene	240	3.1	<b>40</b>	OK*	No Si-O (150 °C)	UV Film Patchy Streaks
2,6-Lutidine	144		<b>32</b>	*		
Quinoline			43	OK	Si-O (150 °C)	
Anisole	154		<b>35</b>	Cloudy (10%)	No Si-O (150 °C)	
Phenylethane	256		<b>39</b>	Cloudy (10%)	No Si-O (150 °C)	
D4 Cyclomethicone		2.4	117	OK	No Si-O (150 °C)	
D5 Cyclomethicone		3.8	17	OK	No Si-O (150 °C)	UV Film Patchy Streaks

\* Limited solubility above 5% or with polymeric silanes

*Italicized viscosity values are from literature, not in-house measurements*

**kovio**

Silane Ink Formulation

# Solvent/Silane Compatibility (Problematic) - 2004

	Solvent	bp (°C)	$\eta$ (cP)	$\gamma$ (mN/m)	Solubility (5 vol%)	FTIR	Thin Film
	D4 Cyclomethicone	24	17.4	OK	No Si-O (150 °C)		
	D5 Cyclomericone	38	17.4	OK	No Si-O (150 °C)	UV Film Patchy streaks	
Exotics	Cineole*	176	2.3	OK→Solids	No Si-O (100 °C)		
	ECC-diobutyl ether	203	14	OK→Solids			
	3-Octanol*	174	7	Cloudy	Oxidation		
	2-Ethylhexanol	182	46	Cloudy	Oxidation		
	Dihydrotetrahydrofuran	208	46	OK	Oxidation		
	Dihydrotetrahydrofuran (HTF)	208	46	OK→Solids			
	Terpinen-4-ol*	212	12	OK	No Si-O (150 °C)	Film oxidation	
	Terpineol*	217	37	32	OK	No Si-O (150 °C)	Film oxidation
	Pine Oil 60		5	OK	Oxidation		

\*Similar results after drying solvent over molecular sieves

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Silane Ink Formulation